U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB-299 252

An Automated Sampler, A Master Analytical Scheme, and a Registry System for Organics in Water

(U.S.) Environmental Research Lab, Athens, GA

1979

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3.
EPA-600/J-79-025	JOURNAL ARTICLE	PB 299252

4. TITLE AND SUBTITLE	5. REPORT DATE
An Automatic Sampler, a Master Analytical Scheme, and a Registry System for Organics in Water	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
A.W. Garrison, J.D. Pope, A.L. Alford, and C.K. Doll*	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Research Laboratory Athens GA 30605 *Midwest Research Institute Kansas City MO 64110	1CC824 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
U.S. Environmental Protection Agency--Athens GA Environmental Research Laboratory College Station Road Athens GA 30605	Journal article 14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES In: Trace Organic Analysis: A New Frontier in Analytical Chemistry
National Bureau of Standards, Gaithersburg MD Pub. No. 519, April 1979. p. 65-78.
Contact: A.W. Garrison, 8-250-3453

16. ABSTRACT

A three-phase analysis program for organics in water is described. In the first phase, a prototype automatic sampler was constructed to sample and concentrate organic compounds from dilute systems, including finished drinking water. The sampler collects and seals up to 26 grab samples for analysis of purgeable organics and perhaps non-volatiles. In the second phase, a general protocol for analytical surveys in which all volatile organics above a specified level in water are identified and quantified will be developed. The master analytical scheme, which incorporates modern GC-MS-computer analytical techniques, should be available in early 1980. Emphasis will be on comparison, selection, and optimization of techniques for sampling, extraction, cleanup, and separation of all gas chromatographable organics in water. In the third phase, a comprehensive data collation and retrieval system for organics in water will be developed. The system, called the Distribution Register of Organic Pollutants in Water (WaterDROP), will include a means for continual updating and dissemination of new information on organics identified in water. WaterDROP will be searchable by several parameters to locate compounds of particular interest to analytical chemists, epidemiologists, enforcement groups, and others.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Chemical analysis Data processing Gas chromatography Organic compounds Sampling Water pollution		07C 68D

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	~~14~~ 16
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE A02-A01

EPA Form 2220-1 (9-73)

EPA-600/J-79-025
JOURNAL ARTICLE

NATIONAL BUREAU OF STANDARDS SPECIAL PUBLICATION 519, Trace Organic Analysis: A New Frontier in Analytical Chemistry, Proceedings of the 9th Materials Research Symposium, April 10–13, 1978, held at NBS, Gaithersburg, Md. (Issued April 1979)

AN AUTOMATIC SAMPLER, A MASTER ANALYTICAL SCHEME, AND A REGISTRY SYSTEM FOR ORGANICS IN WATER

A. W. Garrison, J. D. Pope, and A. L. Alford

U.S. Environmental Protection Agency
Environmental Research Laboratory
Athens, Georgia 30605

C. K. Doll

Midwest Research Institute
Kansas City, Missouri 64110

A three-phase analysis program for organics in water is described. In the first phase, a prototype automatic sampler was constructed to sample and concentrate organic compounds from dilute systems, including finished drinking water. The sampler collects and seals up to 26 "grab" samples for analysis of purgeable organics and concentrates up to 14 samples on various accumulators, such as XAD resins, for analysis of non-purgeable volatiles and perhaps non-volatiles. Samples are collected according to preset sampling frequencies, sequences, flow rates, and collection periods. The sample water is exposed only to Teflon and glass components. The sampler control circuits are AC or DC powered; valving and switching mechanisms are pneumatically operated using bottled gas. The sampler is refrigerated to 4 °C and is capable of unattended operation for up to 7 days in a remote location.

The wide distribution of organics in water emphasizes the need for development of a master analytical scheme that will serve as a general protocol for analytical surveys in which all volatile organic compounds above a specified level in any type of water are identified and quantified. In the second phase, such a scheme, which incorporates modern GC-MS-computer analytical techniques, is currently being developed by the U.S. Environmental Protection Agency (EPA), and should be available in early 1980. In developing the scheme, emphasis will be on comparison, selection, and optimization of techniques for sampling, extraction, cleanup, and separation of all gas chromatographable organics in water. A computer program for quantification will be based upon internal standards selected for each major functional group and volatility class of organics, and upon predetermined recovery and detector response data obtained using several model compounds from each class. The scheme will be tested and improved using samples of surface water, drinking water, and industrial and municipal effluents.

In the third phase, a comprehensive data collation and retrieval system for organics in water will be developed by the EPA. This system, called the Distribution Register of Organic Pollutants in Water (WaterDROP), will include a means for continual updating and dissemination of new information on organics identified in water. WaterDROP will include various chemical and geographical descriptors for each compound, as well as data on concentration, source, analytical method, etc. The data base will reside in computer storage to allow interactive data retrieval by a remote operator and will, in addition be available in a slightly abbreviated cross-indexed printed version. WaterDROP will be searchable by several parameters to locate compounds of particular interest to analytical chemists, epidemiologists, enforcement groups, and others.

Key words: Accumulators; analysis of organics in water; automatic sampler; master analytical scheme; non-purgeable organics; organic pollutant; purgeable organics; WaterDROP.

I. Introduction

Analysis of organic compounds in water begins with sampling, incorporates a comprehensive analytical scheme, and concludes with the interpretation and registration of the data. The U.S. Environmental Protection Agency has begun a three-part program to satisfy these analytical steps. In the first phase, an automatic sampler, designed to sample and concentrate organics from dilute

systems, was constructed. In the second, a master analytical scheme for all volatile organics in all types of water will be developed. To complete the program, a data registry and retrieval system that will incorporate distribution and occurrence records for all specific organic compounds identified in water will be established. This paper describes the development of the program phases.

II. Automatic Sampler

Chemical analysis starts in the field with the collection of a true sample that is representative of the environmental medium of interest. The sampling step for water analysis is complicated in that different types of samples, or different modes of collection, are optimum for different chemical species. For example, no-headspace grab samples are required for purgeable organics [1], whereas large continuous samples are needed for extraction of non-purgeable volatiles by accumulator columns, such as columns of XAD resin [2].

A. Current Sampling Technology

To collect the gamut of volatile (gas chromatographable) organics in water, at least two types of samples are necessary: a no-headspace grab sample for highly volatile, purgeable compounds such as chloroform that are easily lost from the aqueous phase and a grab, composite, or continuous sample for the non-purgeables. Continuous samples are the most representative of the natural environment. No method is presently available for continuous sampling for purgeables, however; the best samples for these compounds is one carefully composited of a series of grab samples. On the other hand, accumulator columns are now available that allow continuous, simultaneous extraction and concentration of many non-purgeable organics from water. Although analytical techniques are sensitive enough to allow detection and identification of sub-microgram-liter concentrations of many compounds in a grab or composited grab sample of 1 to 5 liters, such samples are often not representative. Accumulator columns can provide a representative sample, simultaneous extraction with a high degree of concentration, and low detection limits.

Currently available automatic samplers [3,4] usually are limited to composite (by flow or volume) sampling into a single container. Sample container volume limitations prohibit sampling over a long period, and a sequence of different samples usually cannot be collected. Some other deficiencies of current samplers include: (a) cooling of the sample for preservation over extended periods of time is difficult, (b) contamination can occur from the pump or delivery tube, (c) extreme care is required in transferring collected samples to the laboratory, (d) the sample must be extracted (no accumulators), and (e) purgeable organics are not quantitatively collected.

Columns of activated carbon [5] and other accumulator columns [6] have been used in the field for many years to extract organics from water, but no automatic sampler has been designed especially for the use of accumulator columns. There is no automatic sampler currently available for the collection of water for the analysis of purgeables.

B. The EPA's Automatic Sampler

Midwest Research Institute (MRI), under EPA contract, recently constructed a prototype automatic sampler to meet the specific need for sampling water for purgeable and non-purgeable organics. This new sampler, which is adaptable to both laboratory and field operations, is designed to collect and preserve all types of water samples, including finished drinking water, for analysis of trace organics.

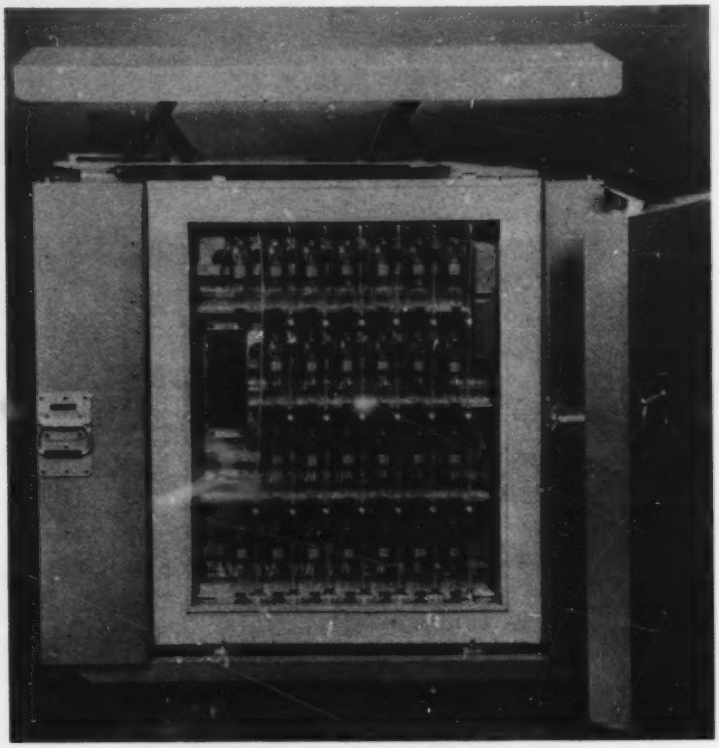


Figure 1. Automatic sampler opened to show the 26 purgeable sample bottles in position.

The sampling system collects 26 purgeable samples (Fig. 1) in special 140-mL sample bottles (Fig. 2) designed to be flushed and filled from the bottom in selected times ranging from 1 to 9 minutes, and then sealed by a rotating Teflon joint. These bottles can be removed from the sampler and their contents transferred to a regular volatile organic analysis (VOA) [1] purging apparatus using gas pressure. Several of these samples can be composited for more representative purgeable analysis or for analysis of non-purgeables by liquid-liquid extraction or other techniques.

The sampler also collects as many as 14 samples on accumulator columns (Figs. 3 and 4) for analysis of non-purgeables. The accumulator column size is variable; the one currently in use holds a 1.8×27-cm column packed with XAD or Tenax resin, activated carbon, or any other accumulator material. The flow rate is adjustable between 50 and 500 mL/min, and each column can be programmed as to volume of water sampled or time span of sample collection. Two or more accumulator columns can be programmed to collect a sample in parallel or in series, and the sequence of columns used can be changed.

The sampler can be operated in a laboratory or a remote site and is capable of unattended operation for up to 7 days. Control circuits are powered by either ac or dc current, the latter using a rechargeable 5 A-h storage battery. Valving and switching mechanisms are pneumatically operated with bottled gas such as propane or compressed air. The sampler is refrigerated to 4 °C, which provides for sample preservation for up to 7 days. The refrigeration system, shown in

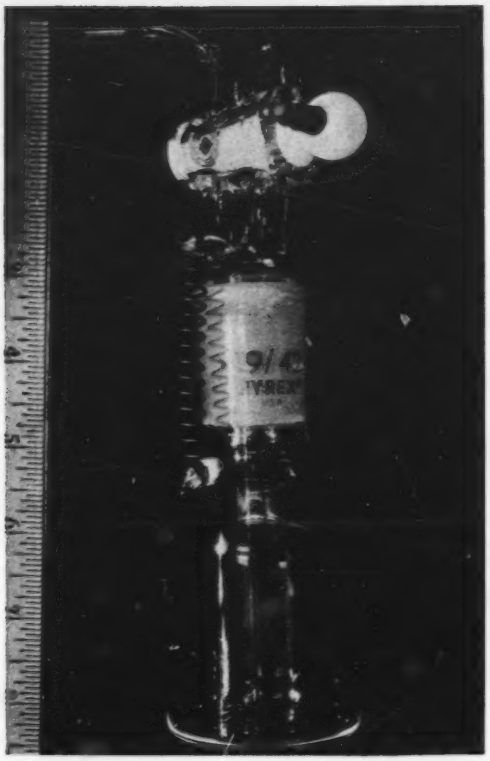


Figure 2. A 140-mL purgeable sample bottle for the automatic sampler.

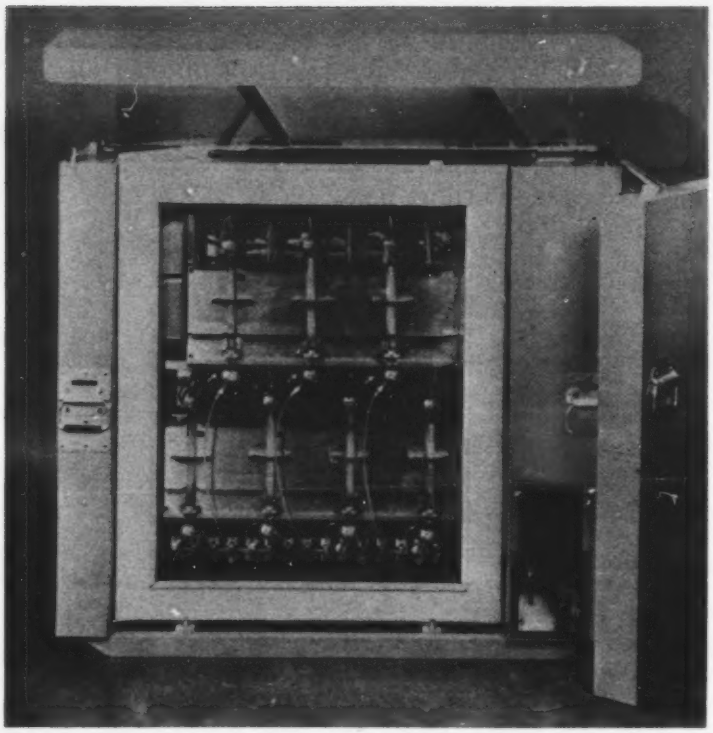


Figure 3. Automatic sampler opened to show 7 of the 14 accumulator columns. Another bank of 7 is located behind the visible bank.

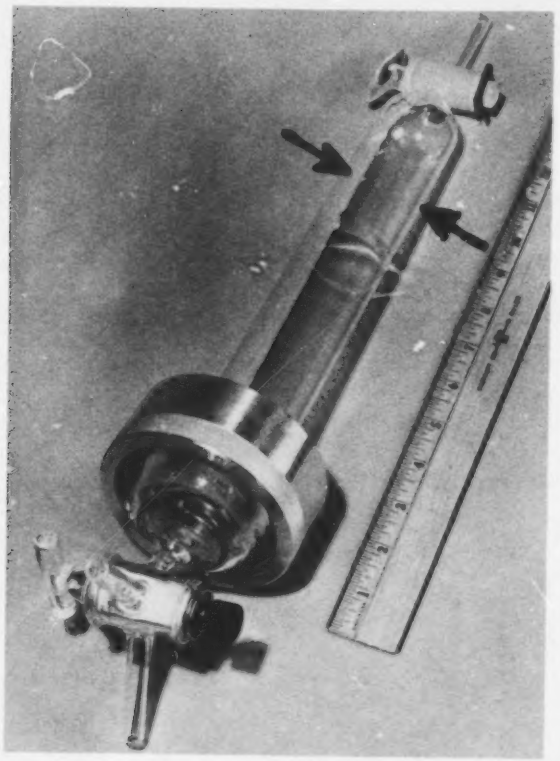


Figure 4. A 1.8×27-cm empty accumulator column for the automatic sampler.

Figure 5, is powered by propane gas (or ac current), being similar to units used in recreational vehicles. To avoid contamination, sample water is exposed only to Teflon and glass components.

The Teflon-bellows sampler pump (Fig. 6), which was especially designed by MRI, is capable of supplying up to 500 mL/min of sample water during the 7-day sampling period. The total sampler unit in its closed and secured configuration is shown in Figure 7.

An endurance test of the battery and the electronic systems representing the worst-case condition indicated that the battery was capable of operating the sampler for 8 days without recharge. The pneumatically operated pump required 55 liters of liquid propane for 7 days of operation at a typical water sample flow rate of 100 mL/min. About 8 liters of liquid propane was required to operate the refrigeration system for 7 days in a 24 °C ambient environment. The sampler temperature did rise to 5 °C on the seventh day, but this is considered acceptable.

The first MRI prototype sampler was received at EPA's Environmental Research Laboratory in Athens, GA, in March 1978 and was immediately subjected to laboratory performance tests. Tests were also begun to evaluate various accumulators that can be used in the sampler. These tests will involve Athens tap water and, later, water at a field site such as a local sewage treatment plant. If the sampler performs as expected, it will be used to sample water from the Great Smoky Mountains National Park, a Biosphere Reserve presently being studied by the EPA's Environmental Monitoring and Support Laboratory, Las Vegas.

This is a first generation automatic sampler. It is obviously overdesigned, especially with regard to the number of individual sample bottles and columns. Thus, the sampler is now too bulky, heavy, and expensive for wide application. The present design should, however, allow a

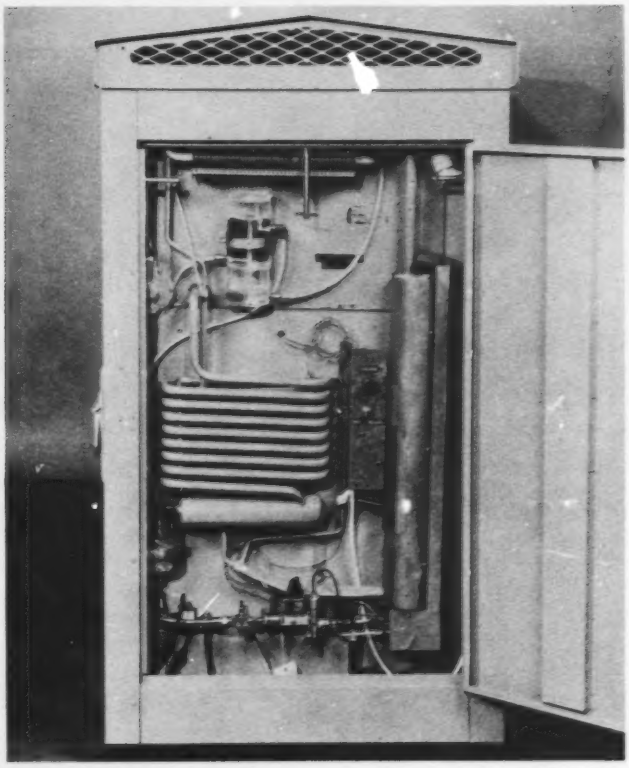


Figure 5. The refrigeration system.

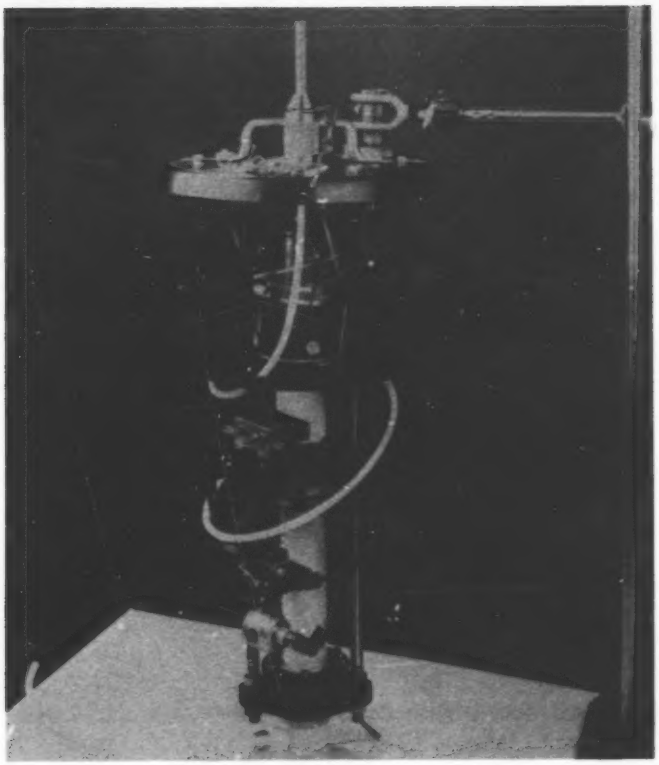


Figure 6. Automatic sampler pump with container removed. Teflon bellows are at the bottom.

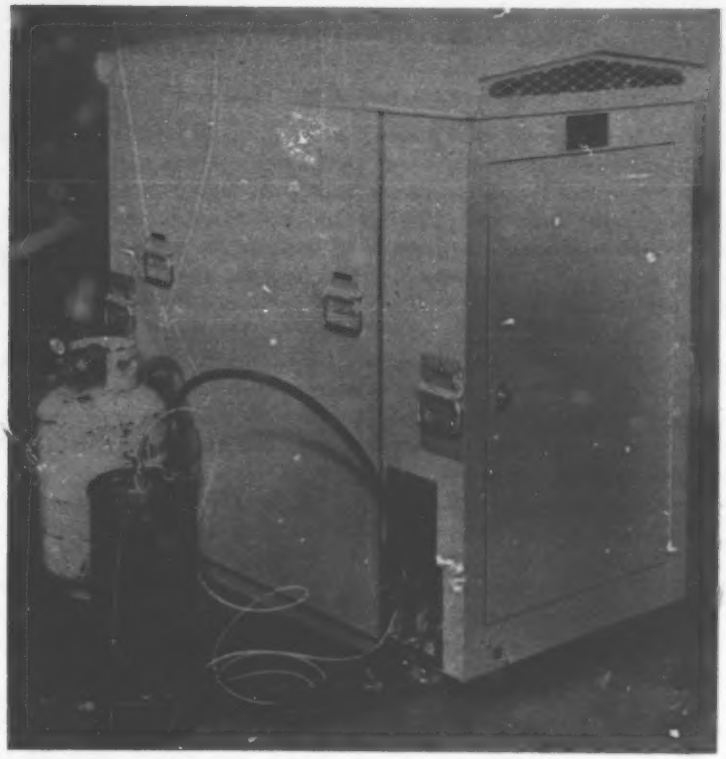


Figure 7. Automatic sampler, closed and secured; dimensions are 134×69×130 cm. Pump is in its black container.

thorough evaluation of the maximum capabilities of an automatic sampler. This evaluation will probably lead to the development of a smaller, lighter, and less expensive sampler that should find wide application.

III. Master Analytical Scheme

Although much effort has been expended by several research groups over the last few years on development of methodology for identification and quantification of selected volatile (gas chromatographable) water pollutants, many gaps still exist. For example, extraction and separation conditions have not been optimized, and the recovery of any identified pollutant is not known without repeating extraction and separation procedures with a standard compound. Internal reference standards have not been selected for all groups or classes of compounds. Specific techniques are available for analyzing many volatile and semi-volatile organics in water, but methods are not comprehensive enough to cover the wide range of functional groups of potential environmental importance.

Several protocols have been written for special situations, but there is a need to draw all the common elements together into a general scheme, incorporating the best of the latest advances in sample preparation and quantification that have been generated piecemeal. In mid-1978, the EPA will award a contract to develop an analytical scheme that, when coupled with modern GC-MS-computer identification techniques, will serve as a general protocol for analytical surveys in which all volatile organic compounds above a specified level are searched for and quantified. The scheme

should be a flexible guide for future work in the analysis of volatile organics in water of all types and be specific enough for ordinary situations, but adjustable by experienced personnel to fit unusually complex samples.

A. Use and Applications of the Master Scheme

In applying the master analytical scheme, the user will be directed how to sample any industrial or municipal effluent, surface water, or drinking water in such a way as to obtain sufficient artifact-free sample for qualitative and quantitative analysis of any organic compound that will pass through a gas chromatograph (GC) or can be derivitized to pass through a GC. Lower detection limits will depend upon compounds being analyzed for and the type of water being analyzed and will be specified in the scheme. Generally, expected detection limits are 0.1 μg/L for drinking water, 1.0 μg/L for surface water, and 10.0 μg/L for effluents. Collection may be by grab sample or accumulator column. The user will be told what internal standards to add, and how and when to add them, for any class of organics. Guidance will be provided in handling and preserving the liquid sample or accumulated organics. Extraction, concentration, and clean-up techniques will be applied as specified by the scheme to allow maximum separation and recovery of the compound or class of compounds of interest to the user, or to allow survey analysis of all organics to which the total scheme applies.

The user will then be directed to use specified gas chromatographic columns and conditions for separation and detection of all compounds of interest, after applying prescribed derivatization techniques when necessary. Once compounds are detected, the user will identify them by previously established GC-MS-computer techniques, then quantify all identified compounds with a computer program developed under this contract. The raw data input to the computer program will consist of retention times of sample components and marker compounds (internal standards), intensities of MS signals for sample components and marker compounds, chemical class of sample components (obtained automatically from an on-line mass spectral search system), sample water type, and volatility class. The computer program will include stored MS detector response factors and recovery factors for marker and model compounds for each class of compound within each volatility fraction for each type of water sample. Figure 8 shows how these stored data will be used to calculate, from the raw data, the estimated concentration of each compound of interest within a

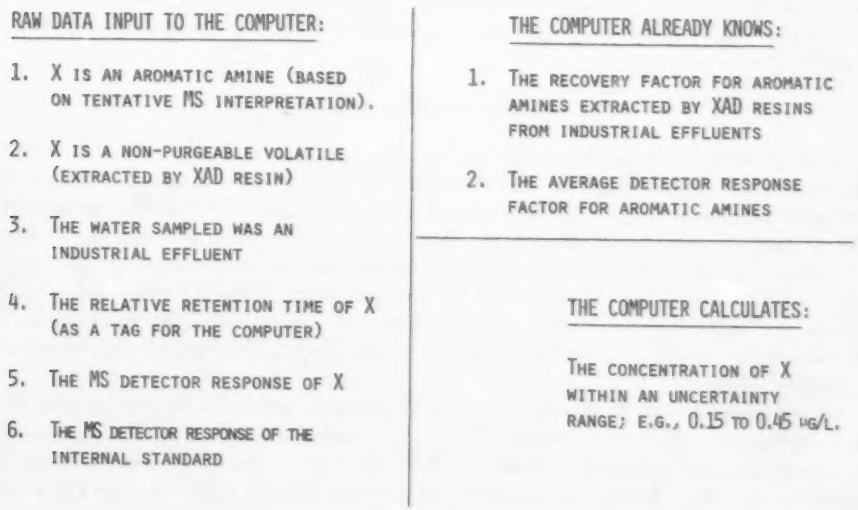

RAW DATA INPUT TO THE COMPUTER:
1. X IS AN AROMATIC AMINE (BASED ON TENTATIVE MS INTERPRETATION).
2. X IS A NON-PURGEABLE VOLATILE (EXTRACTED BY XAD RESIN)
3. THE WATER SAMPLED WAS AN INDUSTRIAL EFFLUENT
4. THE RELATIVE RETENTION TIME OF X (AS A TAG FOR THE COMPUTER)
5. THE MS DETECTOR RESPONSE OF X
6. THE MS DETECTOR RESPONSE OF THE INTERNAL STANDARD
THE COMPUTER ALREADY KNOWS:
1. THE RECOVERY FACTOR FOR AROMATIC AMINES EXTRACTED BY XAD RESINS FROM INDUSTRIAL EFFLUENTS
2. THE AVERAGE DETECTOR RESPONSE FACTOR FOR AROMATIC AMINES
THE COMPUTER CALCULATES:
THE CONCENTRATION OF X WITHIN AN UNCERTAINTY RANGE; E.G., 0.15 TO 0.45 μG/L.

Figure 8. Example of computerized quantitation of compound X using the Master Analytical Scheme.

calculated uncertainty range. The user will apply quality control procedures, as specified by the scheme, during application of the total scheme.

The user will not be bound to use all steps of the scheme, but will be able to select segments appropriate for the analysis of a single selected compound or one class of compound. The scheme will also be flexible enough for the user to adapt it to rapid screening for specific organics with less quantitative accuracy than expected for detailed application, eliminating time consuming techniques designed for unusual functional group classes.

B. Work Necessary for Development of the Scheme

The emphasis of the contractor's experimental work will be on sampling, sample preparation, separation, and quantification. The total scheme will be oriented towards identification and quantification by GC-MS using internal standards. Development of guidelines for the use of marker compounds (internal standards) will be part of the contract; the National Bureau of Standards will assist in the selection of these compounds. Recovery studies will be performed using model systems involving widely varying members of each major functional-group class of organic compound. Extraction techniques will be optimized for each class of compound and each type of water sample, considering the desired level of detection. Accumulator columns will be optimized to collect intermediately volatile compounds. The contractor will be expected to determine optimum GC columns (capillary and packed) and GC conditions for each class or appropriate category of organic compound. State-of-the-art GC-MS-computer systems will be used to detect and identify compounds used in protocol development and to develop techniques for quantification based on internal standards.

Finally, the contractor must prove the protocol by showing its application to a variety of chemical compounds and water types. Spiked and unspiked samples of surface water, drinking water, and industrial and municipal effluents will be specified. (Effluents from energy-related industries will be included.) Model compounds used in recovery studies and compounds for spiking will be based on EPA's priority pollutant list and other chemicals of interest in the water supply program.

The published master scheme is expected to be available in mid-1980.

IV. Distribution Register of Organic Pollutants in Water

The number of organic compounds identified in water is increasing rapidly as scores of laboratories examine effluents, surface water, and drinking water for various reasons. This mass of data needs to be continually updated, classified, and registered to allow development of analytical methodology, to permit accurate health effects studies, and to provide an accurate data base for setting and enforcing pollution regulations.

A. Current Compilations

Shackelford and Keith [7] have published an EPA report listing organic pollutants found in all types of water in North America and Europe. A June 1977 update of this report contained 6944 entries of 1282 different organic compounds. The report contains lists of compounds sorted alphabetically by name, by their location or reference to a published study, and by the type of water in which they were found (29 types are included). It also includes tables that summarize the frequency of occurrence of each compound, the location or reference, and the water type. This list, however, is limited to compounds identified during survey-type analyses. In using these data, one must keep in mind that results of studies that include only analyses for specific compounds are *not* included; polychlorinated biphenyl monitoring studies, for example. Neither does this report include quantitative data.

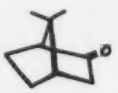
Another valuable compilation of organic compounds found in water is that maintained by the Water Research Centre of England for the Commission of European Communities (CEC) COST-Project 64b [8]. For each compound identified, this listing gives concentrations (if available), type of water sampled, date and location of sample, and reporting laboratory. Compounds are listed by major chemical or use class. Literature searches and regular submissions from laboratories participating in the COST-Project 64b, supplemented by private communications, provide additional entries to this extensive listing. Although the bulk of the compounds listed are those found in western European waters, many data from the U.S. EPA are included. Shackelford and Keith's EPA report [7] includes the CEC data as of October 1975.

B. WATERDROP

A computerized/printed library of organic compounds in water will be the ultimate answer to handling the mass of data described above. In the summer of 1978, the EPA will award a contract for development of a comprehensive collation, registration, and data retrieval system. This system, to be called WaterDROP (Distribution Register of Organic Pollutants in Water) will include a means for continual updating and dissemination of new information on organics in water. It will include various chemical and geographical descriptors for each compound, as well as data on concentration, source, etc. The data base will reside in computer storage to allow interactive data retrieval by a remote operator and will also be available in a slightly abbreviated, cross-indexed, printed version. WaterDROP will be accessible by several modes to search for compounds of particular interest to analytical chemists, epidemiologists, enforcement officials, and others. Figure 9 shows one possible format for WaterDROP data [9].

CAMPHOR

Bornane, 2-oxo
2-Bornanone
2-Camphanone
} Synonyms



Chemical Class: ketone, aliphatic, substituted

C10 H16 O; MW: 152.26; CASRN: 000076222; WLN: L55 A CVTJ A A B

Sampling Date	Sample Site	Conc. (µg/l)	Water Type	Identified By	Lit. Reference	Contact Reference
4-75	Miami, FL (USA)	0.5	Drinking	MS, GC*	1	1
4-75	Cincinnati, OH (USA)	0.1	Drinking	MS, GC*	1	1
4-75	Ottumwa, IA (USA)	0.1	Drinking	MS, GC*	1	1
4-75	Seattle, WA (USA)	0.5	Drinking	MS, GC*	1	1
3-72	Interstate Paper Corp., Riceboro, GA (USA)	90	Waste SIC:2611	MS, GC, IR*	2	1
3-72	Interstate Paper Corp., Riceboro, GA (USA)	20	Waste SIC:2611	MS, GC, IR*	2	1
3-72	Unidentified Kraft Pulp Mill, GA (USA)	45	Waste SIC:2611	MS, GC, IR*	2	1
1-73	Weyerhaeuser Paper Co., Springfield, OR (USA)	400	Waste SIC:2611	MS	3	2
12-73	Weyerhaeuser Paper Co., Everett, WA (USA)	60	Waste SIC:2611	MS	3	2

*Confirmed with a standard

Literature References:

1. R. G. Tardiff, W. L. Budde, W. E. Coleman, J. DeMarco, R. C. Dressman, J. W. Eichelberger, W. H. Naylor, L. H. Keith, R. F. Kopfler, R. D. Lingg, L. McCabe, R. G. Melton, and J. L. Mullaney, "Organic Compounds in Drinking Water: A Five City Study", J. Am. Water Works Assn. (In Press).

2. L. H. Keith, "Analysis of Organic Compounds in Two Kraft Mill Wastewaters", U. S. Environmental Protection Agency Report No. EPA-660/4-75-005, Washington, DC, 1975.

3. B. F. Hrutfiord, T. S. Friberg, D. F. Wilson and J. R. Wilson, "Organic Compounds in Pulp Mill Lagoon Discharge", U.S. Environmental Protection Agency Report No. EPA-660/2-75-028, Washington, DC, 1975.

Contact References:

1. Keith, L. H., Radian Corporation, Austin, TX, 78766, USA. Telephone: (512) 454-4797.

2. Hrutfiord, B. F., College of Forest Resources, Univ. of Washington, Seattle, WA, 98195, USA. Telephone: (206) 543-1714.

Standard Industrial Classification (SIC) Numbers:

2611 Pulp mills.

Figure 9. One possible format for WaterDROP data output.

The data input to WaterDROP will include:

Compound name	Method of identification
Synonyms	Degree of confirmation
CAS Registry Number	Concentration
Wiswesser line notation	Sample site
Empirical formula	Water type
Molecular weight	Sampling date
Chemical class	Literature reference
Structure	Source/laboratory reference
	WaterDROP entry date

The development contract will call for a design phase of 3 months to determine sources of data, methods for evaluation of data, a system for input and continual updating of data, best data output format, necessary computer storage and terminal facilities, the most useful ways to retrieve data from the system, etc. The second contract phase will involve comprehensive data collection from sources throughout the world, evaluation of data to determine quality, collation and storage of the data, development of computer software for data retrieval, and publication of a printed handbook of the data.

It is anticipated that WaterDROP will become part of the Chemical Information System (CIS), a world-wide, publicly accessible chemical information network developed by EPA and the National Institutes of Health. Software for data retrieval will allow the WaterDROP user to query the system for specific compound occurrences according to compound name, geographic area, type of water, molecular structure, CAS Registry Number, and chemical class. If WaterDROP does reside in the CIS, users will be able to interact directly with the other modules of CIS such as Substructure Search, Mass Spectral Search, NIOSH Registry of Toxic Effects of Chemical Substances (RTECS), etc.

The most available product of the WaterDROP contract will be a printed handbook containing all the compound data in the computer files. Manual data retrieval from the handbook will not be as flexible or fast as with the computer system, but suitable indexes will still allow the most useful occurrence data to be located. The handbook will be periodically updated (perhaps every 6 months) with the latest data that has been submitted to the contractor. It is expected that this handbook will be available in the fall of 1979.

V. Conclusions

The automatic sampler, the master analytical scheme, and WaterDROP will all help provide significant advances in our knowledge about trace organics in water. For example, a systematic nationwide survey for specific organics is badly needed in the United States; there is a surprising degree of ignorance regarding the occurrence and distribution of volatile organics, to say nothing of non-volatiles, in water. The analytical advances discussed in this paper should each be applicable to such a survey.

VI. Acknowledgments

Appreciation is expressed to William T. Donaldson, Chief of the Analytical Chemistry Branch (ACB) of the Athens Environmental Research Laboratory, who originated the ideas for the automatic sampler and the master analytical scheme; to Larry Keith, formerly of the ACB staff and now of Radian Corp., Austin, TX, who did much of the original development work on WaterDROP; and to Walter Shackelford of the ACB for his consultation on the master scheme and WaterDROP.

VII. References

[1] Bellar, T. A. and Lichtenburg, J. J., "Determining Volatile Organics at the μg/l Level in Water by Gas Chromatography," *J. Amer. Water Works Assoc.* **66,** 739-744 (1974).

[2] Junk, G. A., Richard, J. J., Fritz, J. W., and Svec, H. J., "Resin Sorption Methods for Monitoring Selected Contaminants in Water," in *Identification and Analysis of Organic Pollutants in Water,* L. H. Keith, Ed., pp. 135-153 (Ann Arbor Science Publishers, Ann Arbor, MI, 1976).

[3] Harris, D. J. and Keffer, W. J., "Wastewater Sampling Methodologies and Flow Measurement Techniques," U.S. Environmental Protection Agency Report No. EPA-907/9-74-005, June 1974, 130 pp.

[4] Lauch, R. P., "A Survey of Commercially Available Automatic Wastewater Samplers," U.S. Environmental Protection Agency Report No. EPA-600/4-76-051, September 1976, 33 pp.

[5] Buelow, R. W., Carswell, J. K., and Symons, J. M., "An Improved Method for Determining Organics by Activated Carbon Adsorption and Solvent Extraction—Part 1," and "...Part II (Test Method)," *J. Amer. Water Works Assoc.*

[6] Dunlap, W. J., Shew, D. C., Scalf, M. R., Crosby, R. L., and Robertson, J. M., "Isolation and Identification of Organic Contaminants in Ground Water," in *Identification and Analysis of Organic Pollutants in Water,* L. H. Keith, Ed., pp. 453-478 (Ann Arbor Science Publishers, Ann Arbor, MI, 1976).

[7] Shackelford, W. M. and Keith, L. H., "Frequency of Organic Compounds Identified in Water," U.S. Environmental Protection Agency Report No. EPA-600/4-76-062, December 1976, 617 pp.

[8] Water Research Centre, "A Comprehensive List of Organic Pollutants Which Have Been Identified in Various Surface Waters, Effluent Discharges, Aquatic Animals and Plants, and Bottom Sediments," Stevenage Laboratory, Elder Way, Stevenage, Hertfordshire SG1 ITH, England, October 1975 (revised 1977).

[9] Keith, L. H., "Distribution Register of Organic Pollutants in Water—An Essential Tool for Environmental Assessment," *Preprints, Division of Environmental Chemistry, American Chemical Society* **16,** 176 (172nd National Meeting, San Francisco, CA, Aug. 29-Sept. 3, 1976).